CHARACTERIZATION OF SPITSBERGEN DISKS BY TRANSMISSION ELECTRON MICROSCOPY AND RAMAN SPECTROSCOPY.

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Introduction: 'Carbonate disks' found in the fractures and pores spaces of peridotite xenoliths and basalts from the island of Spitsbergen in the Norwegian Svalbard archipelago have been suggested to be "The best (and best documented) terrestrial analogs for the [Martian meteorite] ALH84001 carbonate globules ...[1]" Previous studies [1-3] have indicated that Spitsbergen carbonates show broadly comparable internal layering and mineral compositions to ALH84001 carbonate-magnetite disks. We report here for the first time, the detailed mineral characterization of Spitsbergen carbonates and their spatial relationship to the host mineral assemblages in the xenolith, using high resolution TEM (as used previously for ALH84001 carbonate disks [4]). These studies were conducted in concert with complementary Raman and SEM analysis of the same samples. Our results indicate that there are significant chemical and physical differences between the disks in Spitsbergen and the carbonates present in ALH84001.

Methods: Spitsbergen disks are found embedded within a thin translucent white coating that partially covers host mineral grain surfaces (Fig. 1). Since there is very little adhesion of this surface coating to underlying minerals both disks and associated coating can easily be removed using stainless steel surgical tweezers. Three types of disks were selected for analysis based on their apparent color under neutral white light illumination: 'red-maroon', 'red-orange', and 'yellow-orange'. Each was crushed and prepared for ultramicrotomy (Fig. 1) using Embed 812™ epoxy and thin sectioned into 70-100 nm sections using a Reichert MT 7000 ultramicrotome. Sections were analyzed using a JEOL 2000FX operating at 200 keV TEM equipped with a *Si*-drift EDX Noran System 6 detector.

Post-ultramicrotomy, TEM epoxy mounts were coated with ~5 nm of *C* for electron conduction and analyzed using a JEOL 6340 field-emission SEM operating at 15 keV. EDX point spectra and line scans were collected with an IXRF light element detector.

A Horiba Jobin Yvon LabRAM high resolution Raman equipped with an Olympus B41 optical microscope was used to collect *in situ* spot spectra and images. Spectra were acquired from 200–1800 cm^{-1} using a 632.8 nm incident beam and an integration period of 10 s. A *Si* wafer provided by Horiba Jobin was used as a calibration std. (520.56 cm^{-1}) and an Icelandic spar (calcite) was used as a mineral std.

Results: Spitsbergen disks typically range in size from ~20 – 100 μm in diameter and are analogous to that reported for ALH84001 carbonate disks (~10 – 300 μm in diameter; [4]). Concentric oscillatory zoning is apparent under an optical microscope for all disk types, see Fig. 1. An EDX line scan transecting a 'red-orange' disk (Fig. 2) illustrates the chemical zonation of *Si*, *Fe*, *Mg*, & *Ca*, where $[Fe] \propto [Si \oplus Ca]^{-1}$; $[Fe] \propto [Mg]$; and $[Si] \propto [Ca]$. Disks are composed primarily of amorphous, *Si* / *Fe*-rich phase(s) (Figs. 3-4) intermixed with coarse and fine-grain regions of smectite-type phyllosilicates (Fig. 3). Fine-grain crystalline regions of ferrihydrite (Fig. 3) and μm-size areas of mixed cation *Mg-Fe-Ca* carbonate grains (Fig. 4) are dispersed throughout the amorphous matrix; these crystalline phases comprise up to ~20 vol.% of disk material. We found no evidence for either hematite or magnetite. The translucent white coating material consists of one or more *Si* / *Fe*-rich amorphous phases in which are embedded nanoscale mixed cation carbonate (≤ 20 nm) and smectite (≤200 nm) particles.

Raman spectra of *some* disks show the presence of discrete carbonate hotspots (ν_1 sym. stretching mode, Fig. 5) that are not only present within the disks but are also present in the surrounding coating material and corroborate the TEM results. However, we also note that for the majority of disks we found no evidence for any carbonate.

Preliminary Conclusions: Our observations of Spitsbergen disks suggest they are not a good terrestrial analog for ALH84001 carbonates. The Spitzbergen disks appear to be composed primarily of a siliceous, *Fe*-bearing amorphous matrix intermixed with abundant clays, minor ferrihydrite and sporadic regions of *Mg-Fe-Ca* carbonate. In contrast, ALH84001 carbonate disks represent carbonate-magnetite assemblages composed of chemically pure magnetites embedded within and distributed throughout a complex chemically zoned mixed cation (*Fe*, *Mg*, *Ca*, *Mn*) carbonate matrix [4].

References: [1] Treiman A.H. (2005) *LPS XXXVI*, Abstract # 1107. [2] Treiman A.H. *et al.* (2002) *EPSL 204*, 323-332. [3] Steele A. *et al.* (2007) 42, 1549-1566. [4]Thomas-Keprta *et al.* (2009) *GCA* 73,6631-6677.

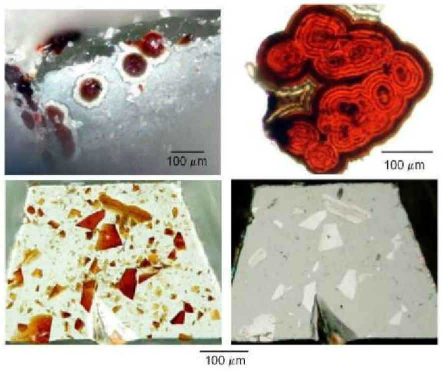

Fig. 1. Upper: Optical views of Spitsbergen red-maroon disks *in situ* (left) and extracted (right) from a xenolith surface. Disks are embedded in a translucent white coating that blankets underlying mineral grains. Lower: Post-ultramicrotomy, optical bright-(left) and dark-field (right) views of crushed disks in a TEM epoxy mount.

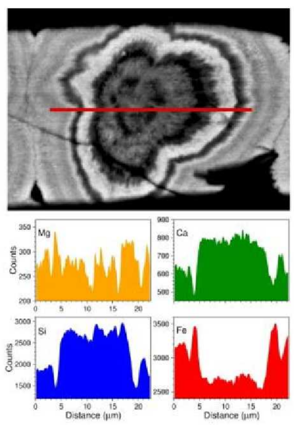

Fig. 2. Upper: BSE image of a red-orange Spitsbergen disk showing the path of EDX line scan data (yellow line) acquired by FE-SEM. Lower: Oscillatory zoning patterns result from variations in *Fe*, *Si*, *Ca*, and *Mg* abundances. Note: oscillatory zoning patterns in Spitsbergen disks are also visible using optical microscopy (see Fig. 1, upper right view).

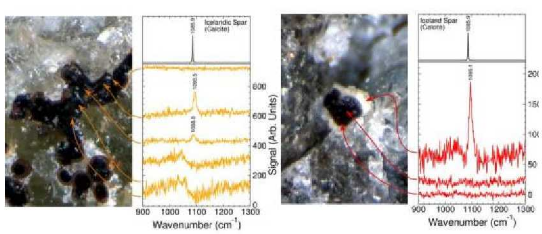

Fig. 5. Optical views of Spitsbergen red-orange (left) and red-maroon (right) disks and their corresponding Raman spectra. Of the five red-orange disks analyzed, only two show peaks consistent with carbonate. Of the three regions analyzed in the red-maroon disks, no carbonate was detected within the disks however it was present in the translucent white coating material.

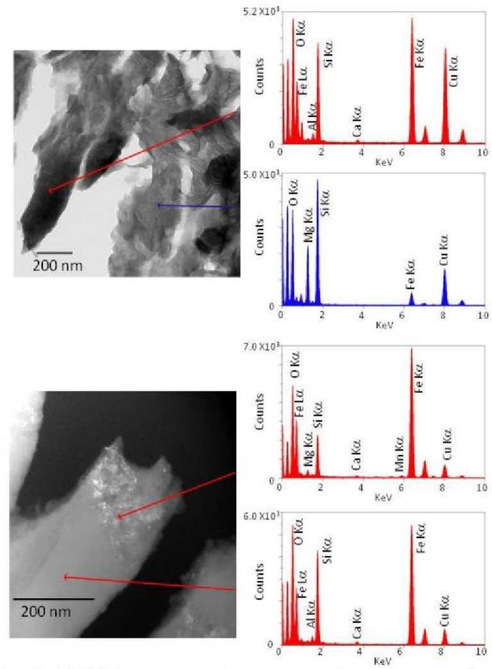

Fig. 3 TEM images and corresponding spectra of sections of red-maroon Spitsbergen disks. Upper: Amorphous regions rich in *Si* & *Fe* (red spectrum) and smectite-type phyllosilicates (blue spectrum). Lower: TEM darkfield image of the siliceous, *Fe*-rich amorphous matrix (gray; lower spectrum with [*Si*]~[*Fe*]) with embedded fine grain ferrihydrite (white regions; upper spectrum with [*Fe*]>[*Si*]).

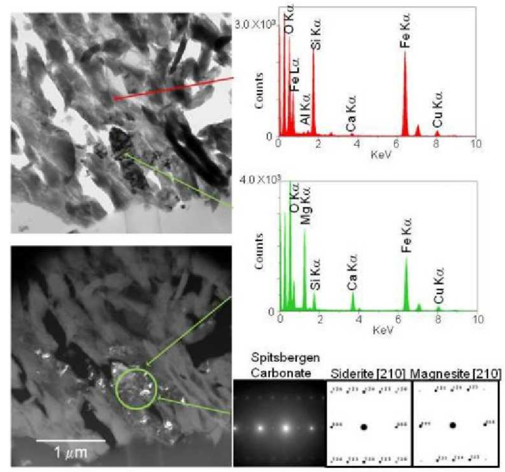

Fig. 4. Bright- (upper left) and dark-field (lower left) TEM views of the same region of a Spitsbergen red-maroon disk thin section. Amorphous material is *Si*-, *Fe*-rich (dull gray areas; red spectrum). Bright regions in dark field indicate the presence of crystalline grains with a composition consistent with *Mg-Fe-Ca* carbonate (green spectrum). SAED of the crystalline region (lower right) is consistent with carbonate.